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Phase exposure-dependent exchange

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Key Points:

- The time-nonlocal mass balance forms are all essentially captured in this theory
- We use a simple generalization of first-order kinetics
- One of the rate coefficients depends on phasic exposure time

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Abstract Solutes and suspended material often experience delays during exchange between phases one of which may be moving. Consequently transport often exhibits combined effects of advection/dispersion, and delays associated with exchange between phases. Such processes are ubiquitous and include transport in porous/fractured media, watersheds, rivers, forest canopies, urban infrastructure systems, and networks. Upscaling approaches often treat the transport and delay mechanisms together, yielding macroscopic "anomalous transport" models. When interaction with the immobile phase is responsible for the delays, it is not the transport that is anomalous, but the lack of it, due to delays. We model such exchanges with a simple generalization of first-order kinetics completely independent of transport. Specifically, we introduce a remobilization rate coefficient that depends on the time in immobile phase. Memory-function formulations of exchange (with or without transport) can be cast in this framework, and can represent practically all time-nonlocal mass balance models including multirate mass transfer and its equivalent counterparts in the continuous time random walk and time-fractional advection dispersion formalisms, as well as equilibrium exchange. Our model can address delayed single-/multievent remobilizations as in delay-differential equations and periodic remobilizations that may be useful in sediment transport modeling. It is also possible to link delay mechanisms with transport if so desired, or to superpose an additional source of nonlocality through the transport operator. This approach allows for mechanistic characterization of the mass transfer process with measurable parameters, and the full set of processes representable by these generalized kinetics is a new open question.

1. Introduction

Upscaled models of macroscopic transport of solutes or suspensions in a wide range of natural or engineered flow systems, including porous or fractured geologic media, watersheds, rivers and open channels, forest canopies, urban infrastructure systems, and networks in general, must capture essential features of advection, diffusion and hydrodynamic dispersion, and delays due to exchange of mass between mobile and immobile phases. Original mathematical modeling of such delay processes in hydrology include the quantification of the mass transfer as a rate-limited first-order kinetic for mobile-immobile exchange [e.g., *Coats and Smith*, 1964], or for ion-exchange [*Nkedi-Kizza et al.*, 1984] or as a spherical-diffusion model of mass exchange between mobile and immobile pore water phases in soil peds combined with macroscopic advective-dispersive transport [*Rao et al.*, 1980]. *Rao et al.* [1980] pointed out that the complexity of the spherical-diffusion model could be simplified by replacing the spherical-diffusion model with a first-order kinetic model, but only if the kinetic rate coefficient was allowed to vary with time. The use instead of a series of first-order exchange rates, each corresponding to an effective subset of the immobile zone porosity or sorption site population was introduced in *Haggerty and Gorelick* [1995], who found how to configure such a "multirate mass transfer" (MRMT) model to mimic not only spherical diffusion but a wide range of cases of mobile-immobile transfers by diffusion. This approach was generalized to an essentially arbitrary distribution of rates in the seminal work by *Haggerty et al.* [2000] who showed, following *Carrera et al.* [1998] that all MRMT models could be cast as integrodifferential ("time-nonlocal") mass balance equations involving a memory function telling how delays impact the spatiotemporal occurrence of solute or suspension undergoing otherwise advective-dispersive transport.

Time-nonlocal transport models are also reached via a separate line of inquiry, that focuses on non-Fickian hydrodynamic dispersion, inspired by seminal works in molecular dynamics of anomalous (diffusive) transport [e.g., *Bouchaud and Georges*, 1990; *Metzler and Klafter*, 2000]. This approach lumps transport in heterogeneous velocity fields with delays due to mass exchange between mobile and immobile states and models the combined process as time-fractional (advective-dispersive) transport (tFADE) [e.g., *Schumer et al*., 2003; *Meerschaert et al*., 2008] or generalized (continuous time) random walks (CTRW) [*Dentz and Berkowitz*, 2003]. There has been a great deal of work examining the relations among these methods and in particular their relevance to the MRMT [*Dentz and Berkowitz*, 2003; *Dentz and Tartakovsky*, 2006; *Berkowitz et al*., 2008; *Zhang et al*., 2009; *Silva et al*., 2009; *Neuman and Tartakovsky*, 2009; *Dentz et al*., 2011; *Zhang et al*., 2014] due perhaps to the generality and simple conceptual basis of the MRMT. We summarize these relations for time-nonlocal forms (to which our study is restricted) here. The CTRW describes transport as a random walk with steps of length *dx* and duration *dt* drawn from a joint density function $\psi(dx,dt)$. If as is commonly assumed these two randomized variables are independent, so that $\psi(dx,dt) = \psi_x(dx)\ \psi_t(dt)$ and if $\psi_x(dx)$ has finite variance, the CTRW is equivalent to the MRMT for macroscopic transport [*Dentz and Berkowitz*, 2003; *Fiori et al*., 2015; *Soler-Sagarra et al*., 2016]. The tFADE is a particular form of the MRMT in which mass-transfer rates are distributed according to a pure power law [*Schumer et al*., 2003] or truncated power law [*Haggerty et al*., 2000; *Meerschaert et al*., 2008; *Zhang et al*., 2014]. It should be noted that the CTRW model that is equivalent to the MRMT (defined above) is a subset of more sophisticated CTRW models, and the tFADE is a subset of a larger set of fractional dynamics models including space-FADE and extended tFADEs [e.g., *Zhang et al*., 2009]. Here we focus only on time-nonlocal transport equations.

All three modeling approaches (MRMT, tFADE, CTRW) have been widely used to simulate both conventional transport with delays due to mobile-immobile partitioning and genuine anomalous (non-Fickian) transport with delays due to correlated residence of solutes or particles in low-velocity regions. When used in this latter fashion, these time-nonlocal transport models "can describe non-Fickian diffusion observed in geological media, but the physical meaning of parameters can be ambiguous, and most applications are limited to curve-fitting." [*Zhang et al*., 2014, abstract]. Specifically, when actual immobilization-remobilization exchange mechanisms are distinct from transport (i.e., independent of the variations in the velocity field) as with MRMT, the lumped approach is an effective or proxy one without a uniquely defined mechanistic basis. Therefore, it is no surprise that the utility of these proxy models in representing the delay mechanism and/or the ability to parameterize the resulting model based on material properties is a matter of continuing debate [e.g., *Neuman and Tartakovsky*, 2009; *Zhang et al*., 2014; *Fiori et al*., 2015; *Neuman*, 2016; *Fiori et al*., 2016] as is the need for time-nonlocal formulations of the transport alone in porous media given sufficient characterization data [*Ginn et al*., 2013; *Lester et al*., 2014; *Heidari and Li*, 2014].

An alternative approach that treats the delay mechanism as completely distinct from the transport operator (as does the MRMT) but that allows for essentially arbitrary remobilization kinetics, is outlined in *Ginn* [2000a, 2009]. This "exposure-time" approach is a mild generalization of conventional first-order kinetics of exchange of mass between phases, in that the remobilization rate coefficient $k_r(\omega)$ depends on exposure time in the immobile phase, or simply time-immobile, ω. We term this "phase exposure-dependent exchange" (PhEDEX) and intend the conceptual framework for any mass exchange process between phases, including diffusive, sorptive, filtration-related, etc. An equivalence relation between this phase exposure-dependent approach and the memory-function formalism is given in *Ginn* [2009]: we expand on that result to show that practically all memory function formulations can be cast as PhEDEX models. This is important because although the memory function approach itself is often equated to an MRMT formulation [e.g., *Silva et al*., 2009], the memory function approach is in fact of broader capability and the two are not equivalent [*Ginn*, 2009]. That is, the time-nonlocal CTRW, tFADE, and MRMT models described above are all subsets of the memory function formulation and so are subsets of the PhEDEX formulation. We show this theoretically and we explore other capabilities of the PhEDEX approach including delay-differential equations and periodic remobilizations such as occur in sediment transport. We introduce a simple finite difference solution to the memory function form with the PhEDEX model and show numerically the PhEDEX model representation of the MRMT gamma and truncated power law MRMT models, as well as the pure power law tFADE model. Like the MRMT, our model is conceptualized at the REV scale and so is a "local" mass transfer model. It is also a linear kinetic due to the first-order nature of the remobilization kinetic. Consequently, it commutes with other nonlinear kinetics and should serve as a useful basis for upscaling multicomponent reactive transport in heterogeneous porous media. Finally, our PhEDEX model explicitly separates the delay mechanism from transport and so allows expression in batch reactor form, allowing for experimental determination of the model parameters, that are the immobilization rate coefficient k_f and the mobilization rate coefficient $k_r(\omega)$ that is a function of time-immobile. These two parameters are mild generalizations of their classical counterparts and detailed further below.

2. The Memory-Function Formalism and Equivalence to PhEDEX

It is now well established that a general way to express transport of a solute or suspended material with volumetric mass, number, or mole density c that undergoes immobilization via diffusion, sorption, or other mechanisms as phase s is captured as a single integrodifferential equation for c [e.g., *Carrera et al.*, 1998; *Haggerty et al.*, 2000; *Schumer et al.*, 2003; *Luo et al.*, 2008; *Silva et al.*, 2009; *Ginn*, 2009; *Zhang et al.*, 2009; *Russian et al.*, 2016]:

$$\frac{\partial c}{\partial t}+L[c]+\beta\frac{\partial}{\partial t}[g*c]=0 \tag{1}$$

where c is $c(\mathbf{x}, t)$ (only time argument is shown), L is a transport operation such as advection-dispersion, "*" indicates convolution in time, g is termed the memory function that is here defined to be the rate of particle immobilization multiplied by the frequency of remaining immobile beyond time t, and it is assumed that $s(\mathbf{x},0)=0$. Assuming zero initial condition in s, the immobilized mass concentration corresponding to (1) is $s=c*g$ and the system is augmented with boundary or initial data on c.

This definition of g follows that of *Ginn* [2009, paragraphs 12 and 17, where other interpretations are described] and has units of s/c. Consequently, here β is defined as a unit conversion factor between c and s phases (units of β are units of c/s) that is otherwise independent of the immobilization process. So, in the case of diffusive mass transfer in porous media where c is in units of mass per mobile-aqueous volume and s is in units of mass per immobile-aqueous volume, β is the ratio of immobile-aqueous to mobile-aqueous porosities; in the case of sorption where c is as above and s is in units of mass per mass bulk volume, β is the ratio of bulk density to mobile aqueous porosity. This structuring of β and g departs from prior models where β incorporates the reaction equilibrium, and isolates the mass transfer process itself entirely within the definition of the memory function g, so that the zeroth moment of g is the equilibrium point of the immobilization-mobilization mass transfer process [*Ginn*, 2009, pgph 12] regardless of the physical definition of the units of c and s, and mass transfer reactions that are not entirely reversible are characterized by a g with an infinite zeroth moment [*Ginn*, 2009, pgph 17].

We begin with a demonstration that all practical integrodifferential transport equations (Fickian or non-Fickian L being a separate issue) with a memory function g can be cast as PhEDEX models. For contiguity of the development (at the cost of doing things in reverse order) we first define parameters of the PhEDEX model from the memory function, and then we develop the PhEDEX model, that involves contiguous time immobilized, ω, as a new independent variable.

We construct a remobilization rate coefficient $k_r(\omega)$ dependent on time-immobile ω from the memory function as shown in *Ginn* [2009, equation (40)]:

$$k_r(\omega)\equiv-\frac{1}{g(\omega)}\frac{dg(\omega)}{d\omega} \tag{2}$$

wherever $g(\omega)$ is nonzero with initial condition

$$k_f\equiv\lim_{\omega\to 0}g(\omega) \tag{3}$$

Because the derivative of $g(\omega)$ is the negative remobilization frequency of all mass immobilized originally at $\omega=0$, and g itself is the mass remaining immobile at ω, the physical meaning of $k_r(\omega)$ is the *fraction* of immobile mass that remobilizes per unit time, as it is in the classical case of constant k_r. Solving for g we obtain $g(\omega)=k_f\exp\left(-\int_0^\omega k_r(\tau)d\tau\right)$ so that $s=c*g$ becomes

$$s(\mathbf{x},t)=\int_0^t\frac{k_f}{v_\omega}c(t-\omega/v_\omega)\exp\left(-\int_0^\omega k_r(\tau)d\tau\right)d\omega\equiv\int_0^t s_\omega(\mathbf{x},t,\omega)d\omega \tag{4}$$

in which ω/v_ω is the (absolute) time at which the mass currently immobile became so, and in which the integrand $s_\omega(\mathbf{x},t,\omega)$ is the solution to the following partial differential equation for $s_\omega(\mathbf{x}, t, \omega)$ that keeps track of time-immobile ω of immobile species s_ω:

$$\frac{\partial s_\omega}{\partial t}+v_\omega\cdot\frac{\partial s_\omega}{\partial \omega}=-k_r(\omega)s_\omega(\omega) \tag{5}$$

that is valid for $\omega>0$ with boundary condition at $\omega=0$ given by $s_\omega(\mathbf{x},t,\omega{=}0)=k_f c(\mathbf{x},t)/v_\omega$, as shown by method of characteristics in *Ginn* [2009]. The "time-immobile" velocity v_ω (termed "exposure-time velocity" in *Ginn* [1999, 2009]) has value 1 and has units of time-immobile per absolute time, and will generally not be carried forward but for when it is needed for clarity on units. The units of $s_\omega(\mathbf{x}, t, \omega)$ are the units of $s(\mathbf{x}, t)$ divided by time-immobile ω, the units of $k_r(\omega)$ are reciprocal absolute time and the units of k_f are the units of β^{-1} times reciprocal absolute time. Equation (5) represents remobilization at rate $k_r(\omega)$ (dependent on time-immobile ω) of s_ω that is immobilized at rate k_f from an aqueous mass concentration c that can be governed by any transport operator L, and we assume mass returning to the mobile phase loses all information associated with time immobilized (this assumption can be relaxed as shown in *Ginn* [1999]), so that

$$\frac{\partial c}{\partial t}+L[c]=-\beta k_f c+\beta\int_0^t k_r(\omega)s_\omega(\omega)d\omega \tag{6}$$

with boundary or initial conditions on c. Equations (5) and (6) are the PhEDEX mass conservation equations for when mass transfer from immobile to mobile phase depends on time-immobile, originally developed in *Ginn* [2000a,b]. This demonstrates that all time-nonlocal mass balance equations can be cast as PhEDEX models when k_f and $k_r(\omega)$ are given and then related to g via (2) and (3). This set includes all MRMT models including cases with singular memory functions where $g(0)$ is not defined as in the tFADE case, as well as additional time-nonlocal forms that cannot be represented as MRMT processes as shown below.

Fernandez-Garcia and Sanchez-Vila [2015] applied the result (2) of *Ginn* [2009] and examined the way it could be used to fit MRMT models, but: (1) did not use the exposure-time concept and instead replaced the immobile-time variable ω with absolute time t as the independent variable of the rate coefficient, (2) required forward and reverse rates (both dependent on absolute time) to be identical, (3) introduced a new "scaling factor" parameter, and (4) used β as an adjustable parameter for particular MRMT functions. We avoid all of these steps, the most critical of which is (1) that resulted in a nonstationary rate coefficient (i.e., a rate coefficient that depends on absolute time) in their model, thus rendering the model itself nonstationary. This is not necessary, and the PhEDEX model presented here is stationary. In any case, several of our results below appear algebraically similar or even identical to results in *Fernandez-Garcia and Sanchez-Vila* [2015], but are fundamentally different because our stationary model puts the remobilization rate in terms of exposure time while immobile, or ω, while their nonstationary model has parameters in terms of time t. Our exposure-time variable ultimately does not increase the dimensionality of the problem (as it does in, e.g., the case of groundwater age distributions, as in *Woolfenden and Ginn* [2009]) because it collapses under the integration in (6) to give us a memory-function formalism that is stationary, allowing one to solve instead the corresponding time-nonlocal form of the PhEDEX, equation (1).

3. Relation Between the PhEDEX Remobilization Rate $k_r(\omega)$ and the Memory Function $g(t)$

As noted above g can be expressed as [*Ginn*, 2009]:

$$g(t)=k_f\exp\left(-\int_0^t k_r(\omega)d\omega\right) \tag{7}$$

that shows us how to construct a memory function given the forward and reverse rates. We will use this later to demonstrate how novel memory functions can be built for nonconventional delays, e.g., periodic, shifted, etc., and their impact on transport with such delays. An alternate form that is sometimes useful [e.g., *Wheeler*, 1997] involves replacing $k_r(\omega)$ with $\int_0^\infty k_r(u)\delta(\omega-u)du$ so that (7) becomes

$$g(t)=k_f\exp\left(-\int_0^t\int_0^\infty k_r(u)\delta(\omega-u)du\,d\omega\right)$$

or

$$g(t) = k_f \exp\left(-\int_0^{\infty} k_r(u)\Phi(t-u)du\right) \tag{8}$$

where $\Phi(t)$ is the Heaviside function that equals 0 for $t < 0$ and 1 for $t \geq 0$. This form makes explicit the memory in g: $\Phi(t-u)$ restricts the integration over all time to only those events occurring at times u prior to the current time t, that is, over history.

4. Classical Case of Constant k_r

With k_r independent of ω, we have conventional first-order (single-site) immobilization-remobilization and (8) becomes

$$g(t) = k_f \exp\left(-k_r \int_0^{\infty} \Phi(t-u)du\right) = k_f \exp(-k_r t) \tag{9}$$

that is the corresponding classical g here allowing for different forward and reverse rates as described in *Ginn* [2009].

5. Equilibrium

In the classic linear sorption case where constant k_r and k_f remain in finite ratio $k_f/k_r \equiv K_d$ but both are very large, the equilibrium retardation coefficient is $[1+\beta K_d]$. Eliminating k_f in favor of K_d in (8) gives

$$g(t) = K_d k_r \exp(-k_r t) = K_d \frac{k_r}{[\exp(t)]^{k_r}} \tag{10}$$

that in the limit as $k_r \to \infty$ is a Dirac's-type function multiplied by K_d as can be seen by integrating over time. Using this in (1) gives

$$[1+\beta K_d]\frac{\partial c}{\partial t} + L[c] = 0 \tag{11}$$

that is the transport equation with classical retardation coefficient corresponding to either diffusive mass transfer (if β is θ_{im}/θ_m) or reversible sorption (if β is ρ_b/θ_m), or other immobilization processes (bacterial adhesion, colloid filtration) by corresponding construction of the units of β, c, and s. It is important to note also that the limit of $g(t)$ in (10) as t goes to zero is $K_d k_r$ and this is true even as k_r goes to infinity. One can construct any Dirac's-type function for $g(t)$ to get this equilibrium limit; and conversely, if $g(t)$ is not Dirac, then the remobilization reaction is not instantaneous and operates as a nonequilibrium reaction.

6. Other Forms Such as the Delay-Differential Mass Transport Equations and Periodic Remobilizations

It is important to note that (5) and (6) form a self-consistent and mass-conservative set of equations for any specification of nonnegative k_f and $k_r(\omega)$. Therefore, they do not need to satisfy (2) and (3), respectively, and can be constructed independently to mimic any mechanistic process that gives rise to reasonable conceptual models of k_f and $k_r(\omega)$, including delayed releases of immobilized mass or periodic remobilizations as might occur in traffic or sediment transport. For instance, in the case where mass is immobilized at rate coefficient k_f and remobilized after a wait-period W, at rate $k_r(\omega) = k_r^o \delta(\omega - W)$ with dimensionless k_r^o then using (5) to solve for $s_\omega(\boldsymbol{x}, t, \omega)$ and then eliminating $s_\omega(\boldsymbol{x}, t, \omega)$ in equation (6) yields:

$$\frac{\partial c}{\partial t} + L[c] = -\beta k_f \left(c(t) - k_r^e c(t-W)\right) \tag{12}$$

where $k_r^e = k_r^o \exp\left(-k_r^o \Phi(0)\right)$ and where $\Phi(0) = 1$ by definition. This shows a delayed (by W time units) return from the immobile phase to the mobile phase at rate equal to $k_f k_r^e$. An example breakthrough curve for this model is presented in Figure 1 using the numerical scheme described in Appendix A, with a Dirac-δ $k_r(\omega)$ approximated as $k_r(\omega) = k_r^o[\Phi(\omega-1) - \Phi(\omega-1.1)]$ with ω in hours, $k_f = 4/hr$ and $k_r^o = k_f$ with transport properties $Pe = 1000$,

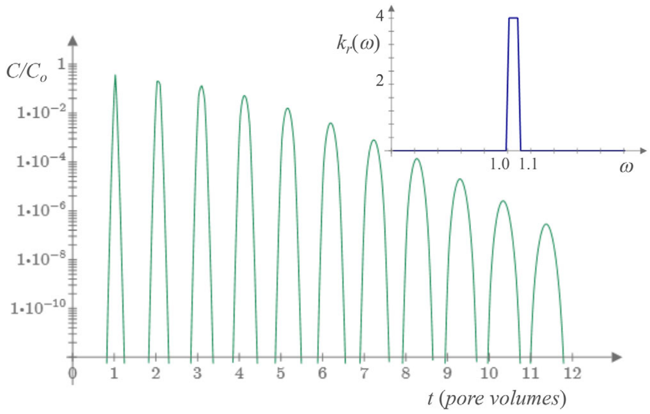

Figure 1. The delay-differential equation breakthrough curve example with k_f and $k_r(\omega)$ (plotted in the inset) as defined in the text, with $\beta=1$, unit advection time v/L, Peclet number $vL/D=10^4$, and unit mass injection.

$L/v=1$ h, $\beta=1$). If mass is remobilized at a rate that fluctuates periodically with time-immobile ω so that for instance $k_r(\omega)=2k_f[sin(5t)+1]$, and remaining parameters as in the foregoing case, the resulting breakthrough curve is as shown in Figure 2.

7. The Age-Immobile Distribution of Immobile Mass Is Explicitly Available for Reactive Transport Calculations

The immobile mass s at any point in $\mathbf{x}$ and t is easily calculated given the history of exposure to c at that point up to time t:

$$s(\mathbf{x},t,\omega)=k_f c(\mathbf{x},t,t-\omega)\exp\left(-\int_0^{\omega}k_r(\tau)d\tau\right) \tag{13}$$

where we have so far assumed the mass is nonreactive beyond the mass transfer reaction. It is possible to incorporate reactions on s by simply adding a reactions source/sink term to (5) and resolving for s. For instance if s undergoes first-order decay at rate λ while in the immobile state, the solution for s is then equation (13) multiplied by $exp(-\lambda\omega)$, and the resulting g is equation (7) multiplied by $exp(-\lambda\omega)$ as well. More realistic reaction kinetics occurring in the immobile phase can be incorporated in (5) as is conventionally done but now using exposure-time immobile instead of absolute time t as the reaction time. Separately, reaction kinetics occurring during time spent in the mobile phase can be added to the mobile phase balance equation (6). Thus the PhEDEX approach allows both mobile and immobile phase age-dependent reactions, where the latter factor into g in the solution (1).

8. PhEDEX Representation of MRMT Models

The classical multirate mass transfer (MRMT) model corresponds to the transport of solute c (units: mass per mobile aqueous volume) in a mobile phase exchanging mass with immobile phase solute s (units: mass per immobile aqueous volume) at distributed first-order mobilization rates α and identical immobilization rates α with $f(\alpha)$ being the frequency distribution of α, which if all immobile domains indexed by α are equally accessible to the mobile phase, can be exactly interpreted as the fraction of immobile porosity domain associated with α. Note that $f(\alpha)=b(\alpha)/\beta$ where $b(\alpha)$ is the immobile zone capacity corresponding to rate α in *Haggerty et al.* [2000]. If there is only one rate α', then $f(\alpha)=\delta(\alpha-\alpha')$, $g(t)$ becomes $=\alpha'\exp(-\alpha' t)$ and the single-rate model [e.g., *Coats and Smith*, 1964; *Nkedi-Kizza et al.*, 1984] is recovered. The corresponding two-phase original transport model [*Haggerty et al.*, 2000] with β factored out of $b(t)$ is

$$\frac{\partial c}{\partial t}+\beta\int_0^{\infty} f(\alpha)\frac{\partial s_\alpha(\alpha)}{\partial t}d\alpha+L[c]=0 \tag{14a}$$

$$\frac{\partial s_\alpha(\alpha)}{\partial t}=\alpha c-\alpha s_\alpha \tag{14b}$$

where s_α is the immobile concentration (subscripted with α here to

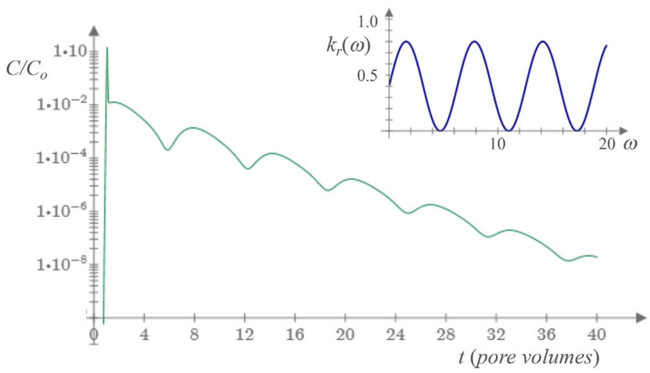

Figure 2. The cyclic release case breakthrough curve with k_f and $k_r(\omega)$ (plotted in the inset) as defined in the text, with $\beta=1$, unit advection time v/L, Peclet number $vL/D=10^4$, and unit mass injection.

distinguish the MRMT from the PhEDEX models) and β is the ratio of total immobile zone porosity to mobile zone porosity. Equations (14a) can be converted to equation (10) as shown in Appendix B, yielding the well-known relation between the memory function and the distribution of MRMT first-order rates

$$g(t)=\int_0^\infty \alpha f(\alpha)\exp(-\alpha t)d\alpha \tag{15}$$

Haggerty *et al*. [2000] tabulated a wide range of memory functions $g(t)$ corresponding to rate distributions $b(\alpha)$ in their Table 1. Here we use (2) and (3), with time-immobile, ω, replacing time, t, as the independent variable in g, to construct PhEDEX model parameters $k_r(\omega)$ and k_f for the principal entries of Table 1 of *Haggerty et al*. [2000] including the first-order rate with different forward and reverse rates ("MRMT2" in *Dentz and Berkowitz* [2003] and *Ginn* [2009]). Whereas *Haggerty et al*. [2000] maintain β within their definition of g, we have factored it out and accounted for it as a separate factor in (1) and so it does not appear in our table. Its definition can vary per case and in the MRMT in general it is defined as $\theta_{im}R_{im}/\theta_m R_m$ to accommodate equilibrium sorption in addition to the context of diffusive mass transfer of *Haggerty et al*. [2000]. The truncated power law case is treated separately later on.

As noted in many prior works, all the gamma, power law, and infinite diffusion models generate late-time solutions to c that are proportional to $t^{-(power+1)}$, where *power* is $\eta+1$ for the gamma-distributed rate model case; γ for the pure power law case; and 3/2 for the infinite diffusion case. For these cases, and for the truncated power law case (below), the PhEDEX mobilization rate is proportional to *power*/ω, with the impact of *power* restricted to a multiplicative constant. Figure 3 shows replications of the breakthrough curves for the parameters corresponding to the gamma-distributed late-time approximation (thus the discrepancy at early time) MRMT of *Haggerty et al*. [2000, Figure 2] using the numerical scheme described in Appendix A.

The results for the pure power law distributed rate model and for all the diffusion models involve undefined forward rate k_f and remobilization rate $k_r(\omega)$ that is singular at the origin, as is the memory function corresponding to these cases. This corresponds to a mass transfer reaction that is effectively instantaneous at early exposure time ω, and is handled by assigning the corresponding density of g to an equilibrium reaction. For brevity, this is done only for the tFADE case in this paper but the same approach would be used for the diffusion cases. The three classical diffusion cases (finite layer, cylinder, sphere) all have rapidly converging series representations for $k_r(\omega)$, and deserve further inspection as indicated by the analogous results in *Fernandez-Garcia and Sanchez-Vila* [2015] who explore how their nonstationary rate coefficient $\omega(t)$ (analogous to our $k_r(\omega)$) decreases as $1/t$ until an asymptote is reached and link this to the aforementioned results from *Rao et al*. [1980].

9. PhEDEX Representation of Non-MRMT Models

Equation (15) shows that, as pointed out in *Haggerty et al*. [2000], the MRMT memory function is the Laplace transform with respect to α of $\alpha f(\alpha)$. Thus, given a time-nonlocal mass balance with memory function $g(t)$, there is a corresponding MRMT model only if (1) the inverse Laplace transform of the integral of $g(t)$ exists and (2) the corresponding rate distribution $f(\alpha)$ has the properties of a probability distribution, i.e., is nonnegative and integrates to unity. This latter requirement (that is easier to test than the former) translates into the restriction that MRMT models can only represent memory functions $g(t)$ that integrate to unity, as can be seen by integrating equation (15) over all time (alternatively if β not factored out of g, then MRMT g's must integrate to β). This is not required in the PhEDEX formalism that only requires nonnegative k_f and $k_r(\omega)$ so that $g(t)=k_f\exp\left(-\int_0^t k_r(\tau)d\tau\right)$ per equations (2) and (3). Because k_f is independent of $k_r(\omega)$, there are no such restrictions on the PhEDEX g, and this shows that there is a large class of PhEDEX models that generate memory functions that do not fit within the MRMT paradigm, including for instance the PhEDEX model underlying Figure 1.

10. PhEDEX Representation of Truncated Power Law (TPL) Delays

The TPL model holds that the distribution of rates is proportional to a power of the rate as long as the rate is within a specified interval, and zero otherwise. For notational consistency, we apply the TPL as described in *Haggerty et al*. [2000]:

$$b(\alpha)=\begin{cases} C_k\alpha^{k-3} & \alpha_{\min}<\alpha<\alpha_{\max} \\ 0 & otherwise \end{cases} \tag{16}$$

Table 1. Catalogue of MRMT Models With Corresponding Memory Functions $g(t)$ and PhEDEX Parameters

MRMT Model	$g(t)$	$k_r(\omega) \equiv \frac{-1}{g(\omega)}\frac{dg(\omega)}{d\omega}$	$k_f \equiv lim_{\omega\to 0}\ g(\omega)$
First-order	$\alpha' \exp(-\alpha' t)$	α'	α'
First-order with forward rate α_f, reverse rate α_r	$\alpha_f \exp(-\alpha_r t)$	α_r	α_f
Discrete multirate[a]	$\sum_{j=1}^{N} f_j \alpha_j e^{-\alpha_j t}$	$\frac{\sum_{j=1}^{N} f_j \alpha_j^2 e^{-\alpha_j \omega}}{\sum_{j=1}^{N} f_j \alpha_j e^{-\alpha_j \omega}}$	$\sum_{j=1}^{N} f_j \alpha_j$
Continuous multirate[a]	$\int_0^\infty \alpha f(\alpha) e^{-\alpha t} d\alpha = \mathcal{L}\{\alpha f(\alpha)\}$	$\frac{\mathcal{L}\{\alpha^2 f(\alpha)\}}{\mathcal{L}\{\alpha f(\alpha)\}}$	$\int_0^\infty \alpha f(\alpha) d\alpha$
Gamma (γ, η) distribution	$\gamma\eta(\gamma t+1)^{-(\eta+1)}$	$\frac{\eta+1}{\omega+1/\gamma}$	$\gamma\eta$
Pure power law distribution (time-fractional ADE)[b]	$\frac{t^{-\gamma}}{\Gamma(1-\gamma)},\ 0<\gamma\le 1$	$\frac{\gamma}{\omega}$	∞[f]
Diffusion: infinite layer[c]	$\frac{R_{im}\theta_{im}a_w}{R_m}\sqrt{\frac{D_a}{\pi t}}$	$\frac{1}{2\omega}$	∞
Diffusion: finite layer[d]	$2c\sum_{j=1}^{\infty} e^{-\frac{\pi^2 c}{4}(2j-1)^2 t}$	$\frac{\pi^2 c}{4}\frac{\sum_{j=1}^{\infty}(2j-1)^2 e^{-\frac{\pi^2 c}{4}(2j-1)^2\omega}}{\sum_{j=1}^{\infty} e^{-\frac{\pi^2 c}{4}(2j-1)^2\omega}}$	∞
Diffusion: cylinder[e]	$4c\sum_{j=1}^{\infty} e^{-u_j^2 ct}$	$c\frac{\sum_{j=1}^{\infty} u_j^2 e^{-u_j^2 c\omega}}{\sum_{j=1}^{\infty} e^{-u_j^2 c\omega}}$	∞
Diffusion: sphere	$6c\sum_{j=1}^{\infty} e^{-j^2\pi^2 ct}$	$\pi^2 c\frac{\sum_{j=1}^{\infty} j^2 e^{-j^2\pi^2 c\omega}}{\sum_{j=1}^{\infty} e^{-j^2\pi^2 c\omega}}$	∞

[a] f_j (or $f(\alpha)d\alpha$) is the frequency of occurrence of discrete rate α_j (or of continuous rate α).
[b] See subsequent section for truncated power law cases.
[c] R_{im} is the immobile zone retardation factor, R_m is the mobile zone retardation factor, θ_{im} is the matrix porosity, a_w is the immobile zone specific surface area.
[d] c is D_a/a^2 where D_a is an apparent diffusivity and a is a layer thickness.
[e] u_j is the jth root of the Bessel function of a first kind of zeroth order.
[f] Unbounded k_f cases corresponds to equilibrium mass transfer, described in text for tFADE case.

where the normalizing constant C_k is $(k-2)/(\alpha_{\max}^{k-2}-\alpha_{\min}^{k-2})$ when $k\neq 2$ and is $1/[\ln(\alpha_{\max})-\ln(\alpha_{\min})]$ when $k=2$. In this case

$$g(t;k)=\frac{C_k}{t^{k-1}}(\gamma(k-1,\alpha_{\max}t)-\gamma(k-1,\alpha_{\min}t)) \tag{17}$$

where

$$\gamma(k-1,x)\equiv\int_0^x y^{k-2}\exp(-y)dy$$

is the lower incomplete gamma function. Via equation (2) we obtain the mobilization rate as a function of time-immobile for the general case $k>1$:

$$k_r(\omega;k)=\frac{k-1}{\omega}-\omega^{k-2}\frac{\alpha_{\min}^{k-1}\cdot\exp(-\alpha_{\min}\omega)-\alpha_{\max}^{k-1}\exp(-\alpha_{\max}\omega)}{\gamma(k-1,\alpha_{\min}\omega)-\gamma(k-1,\alpha_{\max}\omega)} \tag{18}$$

The first term on the right-hand side of (18) is the same as that for the pure power law (with the parameter γ of the pure power law replaced by $k-1$), and the second term is the correction due to the truncation that fixes the limits of $k_r(\omega;k)$ at values of ω outside of the rate interval $[\alpha_{\max},\alpha_{\min}]$. With use of L'Hôpital's rule for the cases $k>1$ we find $lim_{\omega\to 0}\ k_r(\omega)=[(k-1)(\alpha_{\max}^k-\alpha_{\min}^k)]/[k(\alpha_{\max}^{k-1}-\alpha_{\min}^{k-1})]$, and for the $k=1$ case we have $lim_{\omega\to 0}\ k_r(\omega)=(\alpha_{\max}-\alpha_{\min})/\ln(\alpha_{\max}/\alpha_{\min})$ (with single application of L'Hôpital's rule). While the results for the $k>1$ cases are all the same, one must perform the limit separately for the case $k=2$ because L'Hôpital's rule can only be used once there, as with the $k=1$ case. At the other end, the $lim_{\omega\to\infty}\ k_r(\omega)=\alpha_{\min}$ in all cases. Finally, the PhEDEX forward rate k_f is got from (3) as follows: $k_f\equiv lim_{t\to 0}\ g(t)=lim_{t\to 0}\ \frac{C_k}{t^{k-1}}\left(\int_{a_{\min}t}^{a_{\max}t} y^{k-2}e^{-y}dy\right)=C_k\left(\int_{a_{\min}}^{a_{\max}} u^{k-2}du\right)=\frac{C_k}{k-1}(a_{\max}^{k-1}-a_{\min}^{k-1})$, via change

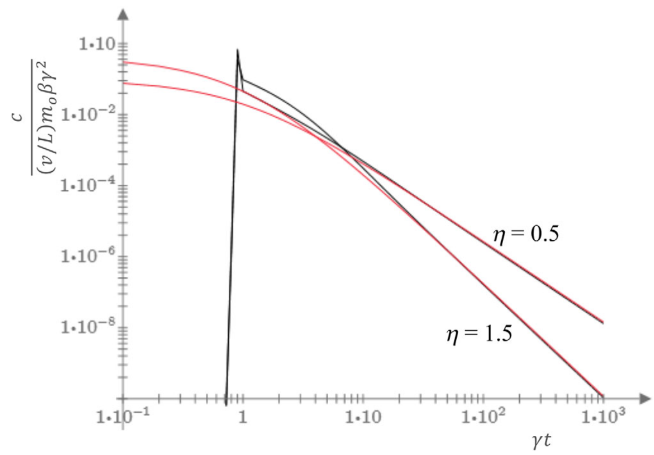

Figure 3. The PhEDEX model (black curves) of the MRMT gamma-distributed rate cases $\eta = 1/2$ and $\eta = 3/2$ for general γ (late-time solution equation (23) of *Haggerty et al*. [2000] as shown in **red**) with k_f and $k_r(\omega)$ as defined in the text and other properties corresponding to Figure 2 of *Haggerty et al*. [2000]; $\beta = 1$, unit advection time *v/L*, Peclet number $vL/D = 10^4$, and unit mass injection.

of variables $y = ut$. Using these results, we duplicate the breakthrough curves of Figure 4 of *Haggerty et al*. [2000] for the conditions therein, using the numerical scheme described in Appendix A, in Figure 4.

11. PhEDEX Representation of the Time-Fractional Advection-Dispersion Equation (tFADE)

As noted above, if $g(t)$ is not Dirac, then the remobilization reaction is not instantaneous and operates as a nonequilibrium reaction. If the forward rate of immobilization k_f is large enough, then we have a case where mass is always shifting from the mobile to the immobile phases and no equilibrium will be reached. This is exactly the tFADE case as pointed out in *Schumer et al*. [2003] and the numerous subsequent works on the original tFADE model, where $g(t)=t^{-\gamma}/\Gamma(1-\gamma)$. In this case, application of (2) gives $k_r(\omega) = \gamma/\omega$ (analogous to the time-dependent k_r in *Fernandez-Garcia and Sanchez-Vila* [2015], and (3) gives k_f unbounded. For numerical solution it is useful to write (7) as the limit:

$$g(t)=\frac{t^{-\gamma}}{\Gamma(1-\gamma)}=\lim_{\varepsilon\to 0} k_f(\varepsilon)\exp\left(-\int_{\varepsilon}^{t}\frac{\gamma}{\omega}d\omega\right) \tag{19}$$

For t close to ε, the exponential is $\sim$1 and we can then approximate (3) as

$$g(\varepsilon)=\frac{\varepsilon^{-\gamma}}{\Gamma(1-\gamma)}\equiv k_f(\varepsilon) \tag{20}$$

In application ε is finite and the error in this approximation is that for $t \in [0, \varepsilon]$ $g(t)$ is replaced by $g(\varepsilon)$; the lost density of $g(t)-g(\varepsilon)$ over this interval corresponds to very fast transfers, which we approximate as an equilibrium reaction. This lost density is shown in Appendix C to add up to an area A, and we correct for this error by adding to g of (19) a Dirac's function with area A and argument t. This attributes the lost density of g as if it were an equilibrium reaction, and results in a retardation factor multiplying the first term of equation (10) equal to $1+\beta A$. Details of this approach and calculation of A are given in Appendix C. We use this approach in our numerical solution

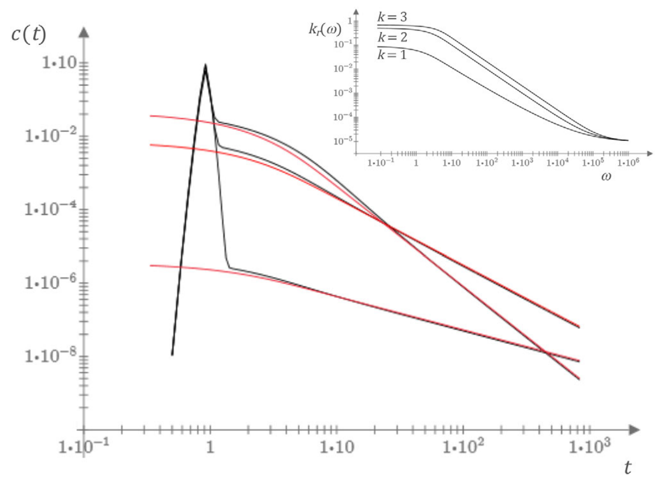

Figure 4. The PhEDEX model (black curves) of the MRMT truncated power law-distributed rate for cases $k = 1$, 2, and 3 (late time solutions equations (31), (32), and (33), respectively, of *Haggerty et al*. [2000] as shown in **red**) breakthrough curves with k_f and $k_r(\omega)$ (shown as the inset) as defined in the text and all other properties corresponding to Figure 4 of *Haggerty et al*. [2000]; $\beta = 1$, $\alpha_{min}=10^{-5}$, $\alpha_{max}=1$, unit advection time *v/L*, Peclet number $vL/D = 10^4$, and unit mass injection.

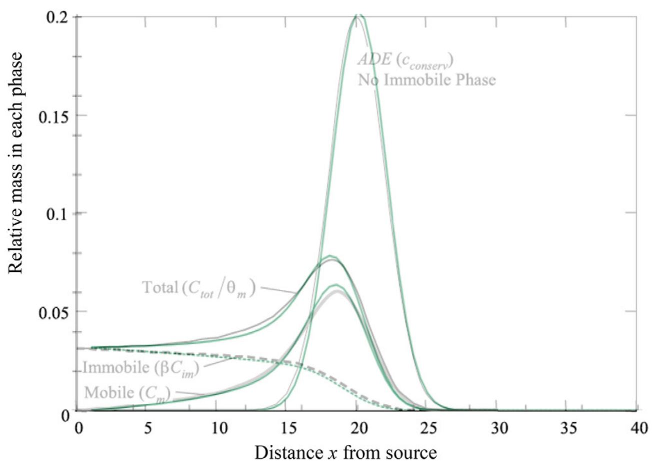

Figure 5. The PhEDEX model of the tFADE case profile curves of Figure 1 of *Schumer et al.* [2003] with k_f and $k_r(\omega)$ as described in Appendix C and all other properties corresponding to Figure 1 of *Schumer et al.* [2003]; $v=1$, $t=20$, $D=0.1$, $\beta=0.1$, $\gamma=0.3$.

described in Appendix A with $\varepsilon=\Delta t/2$, to duplicate Figures 1 and 5 of *Schumer et al.* [2003] as shown in Figures 5 and 6. The retardation factor R for these conditions is 1.013 and is handled in these simulations by obtaining the profiles (Figure 5) at time tR, and by rescaling the time axis as tR for the breakthrough curve (Figure 6). Despite the near-unity value of R, the retardation leads to a clear error if unaccounted for in these simulations because the transport is at a high Peclet number (10^4).

If the tFADE parameter γ is unity, the entire tFADE g becomes a Dirac function as noted in *Schumer et al.* [2003]: the tFADE equilibrium case is reached as $\gamma \to 1$ because $g(t)=t^{-\gamma}/\Gamma(1-\gamma)$ becomes a Dirac's function in that limit, and (1) gives an equilibrium retardation coefficient with value $[1+\beta]$, e.g., the tFADE $K_d=1$. This same result is found with our approximation as is shown by taking the limit as $\gamma \to 1$ of (19) (with $k_f(\varepsilon)$ given by (20)):

$$\lim_{\gamma\to 1}\frac{\varepsilon^{-\gamma}}{\Gamma(1-\gamma)}\exp\left(-\int_{\varepsilon}^{t}\frac{\gamma}{\omega}d\omega\right)=\lim_{\gamma\to 1}\frac{\varepsilon^{-\gamma}}{\Gamma(1-\gamma)}\left(\frac{t}{\varepsilon}\right)^{-\gamma}=\lim_{\gamma\to 1}\frac{t^{-\gamma}}{\Gamma(1-\gamma)} \tag{21}$$

Note that one can generalize the tFADE to accommodate nonunity K_d (without attributing reaction issues to the independently measurable β) by simply replacing $k_f(\varepsilon)$ with $K_d k_r(\varepsilon)$ and proceeding again through (19)–(21), yielding equilibrium retardation coefficient $[1+\beta K_d]$.

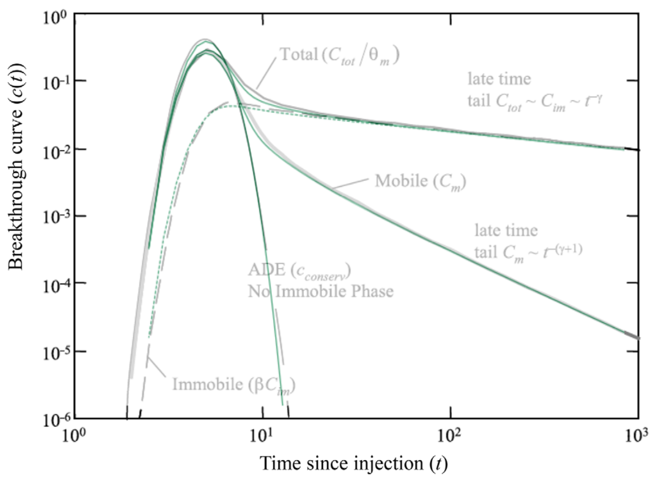

Figure 6. The PhEDEX model of the tFADE case profile curves of Figure 5 of *Schumer et al.* [2003] (overlain on a copy of that figure) duplicated with k_f and $k_r(\omega)$ as described in Appendix C and all other properties corresponding to Figure 1 of *Schumer et al.* [2003]; $v=1$, $x=5$, $D=0.1$, $\beta=0.1$, $\gamma=0.3$.

12. Conclusions

Evidence that residence-time in phase can serve as a fundamental variable controlling effective kinetics is available from research ranging from diffusive mass transfer in soils [*Rao et al.*, 1980] to colloid filtration [*Dabros and Van de Ven*, 1982] to mineralogical [*Glassley et al.*, 2002] or biochemical [*Sanz-Prat et al.*, 2016] heterogeneity. The exposure-time approach [*Ginn*, 1999] provides one avenue toward the development of models to account for these effects. Here we keep track of exposure time while immobile (or simply, time-immobile) as a way to account for delays during transport and show that the integro-differential mass balance equation corresponding to generically time-nonlocal transport can be cast as a PhEDEX process whenever equations (2) and (3) can be solved, including approximately cases of singular memory functions such as the tFADE case where the solution to (3) is undefined. The basic assumptions in the PhEDEX model are that both immobilization and remobilization are first-order (linear) processes, with a constant immobilization rate coefficient and a remobilization rate coefficient that depends on time spent immobile, and the two rate coefficients are independent of one another. The approach focuses on mechanistic delay and is not constructed as a paradigm for handling delays associated with the transport, e.g., preasymptotic dispersion or quasi-ballistic transport, but, as should not be surprising from the common capabilities of the alternative time-nonlocal formulations in this regard, could be used to mimic those processes in an upscaling context.

This work explores a novel means of construction of time-nonlocal mass balance expressions, and, informed by the results of *Carrera et al*. [1998], *Haggerty et al*. [2000], and *Schumer et al*. [2003], among others, connects the PhEDEX approach back to alternative nonlocal formulations. Mathematically, the PhEDEX approach is a more general alternative to the MRMT and its corresponding tFADE or CTRW forms, and shares several advantages with the MRMT approach. Both methods are spatially local, testable by batch experiments on mass exchange without advective-dispersive transport, mathematically relatively straightforward requiring only calculus and differential equations, and linear, allowing for superposition of reaction kinetics in either mobile or immobile phases. Therefore, both serve as a potential upscaling basis for reactive transport [e.g., *Ma et al*., 2010; *Soler-Sagarra et al*., 2016, and references cited therein; *Sanz-Prat et al*., 2016]. The transport operator is unrelated to the mass exchange models and so can be independently specified as Fickian or non-Fickian. While both involve an additional dimension, both collapse this additional dimension into a convolution of the form (1) so that it does not increase the dimensionality of simulation strategies for c.

Further advantages to the PhEDEX approach are its more general relation to memory functions and its explicit use of time-immobile as opposed to (distributed) rate of mass transfer as independent variable. The PhEDEX approach can be cast for practically any memory function while the MRMT rate distribution $f(\alpha)$ exists only if (1) the inverse Laplace transform of the integral of $g(t)$ exists, and (2) the integral of $g(t)$ is unity. PhEDEX formulations for delay-differential equations and for essentially arbitrarily specified remobilization rates are possible as demonstrated. Some examples shown here reflect non-Markovian remobilizations that depend on waiting times between entrainment: this is recognized as a promising avenue for future research in sediment transport [e.g., *Schumer et al*., 2009]. The explicit treatment of time-immobile as opposed to distributed rate as an independent variable allows direct use of data on remobilization dynamics without requiring the introduction of an effective rate model, as originally suggested in *Rao et al*. [1980].

Appendix A: Numerical Solution

The extra dimension of exposure time in the PhEDEX model (5) and (6) is not a problem computationally because it collapses naturally to overlay the time dimension through the convolution in equation (5) and this provides the simplest avenue to solution. Equation (10) after differentiation of the convolution

$$\frac{\partial c}{\partial t}+\beta\left[c*\frac{\partial g}{\partial t}\right]+L[c]=-\beta g(0)c(\boldsymbol{x},t) \tag{A1}$$

is an integrodifferential equation that is easy to solve with explicit finite differences, demonstrated here for the one-dimensional (space) case. First, we replace the derivative of the PhEDEX memory function with its explicit derivative

$$\frac{dg}{dt}=-k_f k_r(t)\exp\left(-\int_0^t k_r(\omega)d\omega\right)\equiv -k_f f(t) \tag{A2}$$

and use (3), with which (A1) becomes

$$\frac{\partial c}{\partial t}-\beta k_f\int_0^t f(\tau)c(t-\tau)d\tau+L[c]=-\beta k_f c(x,t) \tag{A3}$$

The term on the right-hand side is recognized as the first-order immobilization that originally appeared in (6). The convolution kernel f can be calculated prior to solution and the function $c(t-\tau)$ in an explicit scheme has already been calculated and is merely retrieved during the course of the solution. For present purposes, we assume without loss of generality advective-dispersive transport and for simplicity the one-dimensional case with steady velocity, so that $L[c]=v\frac{\partial c}{\partial x}-D\frac{\partial^2 c}{\partial x^2}$. A convenient dimensionless form is obtained with $T\equiv\frac{tv}{L}$, $X\equiv\frac{x}{L}$, $K_f\equiv\frac{k_f}{\theta_m}\frac{L}{v}$, $F(u)\equiv\frac{L}{v}f\left(u\frac{L}{v}\right)$, and $C(X,T)\equiv c\left(XL,T\frac{L}{v}\right)$, where L is a characteristic length of advective transport, which gives

$$\frac{\partial C}{\partial T}(X,T)-K_f\int_0^T F(u)C(X,T-u)du+\frac{\partial C}{\partial X}-\frac{1}{Pe}\frac{\partial^2 C}{\partial X^2}=-K_f C(X,T) \tag{A4}$$

Solving (A4) by explicit cell-centered finite differences, using forward-time, backward space for the advective component, the convolution, and the first-order immobilization term on the right-hand side, with unit Courant number so that $\Delta x=v\Delta t$, and time-centered, central difference in space dispersive flux, yields the following expression for the value of $C_{i,j}$, the value of mobile zone concentration in cell (i, j), where i indices space X and j indices time T, initial condition data are placed in $j=0$ and boundary condition data are placed in $i=1$ with $i=0$ an identical ghost row to prevent upstream dispersion. The recursion template is

$$C_{i,j}=C_{i-1,j-1}+D_p\left[C_{i-2,j-1}-2C_{i-1,j-1}+C_{i,j-1}\right]+\sum_{k=0}^{j-1}F_k C_{i-1,j-1-k}-K_{fo}C_{i-1,j-1}$$

where $D_p=\frac{\Delta t}{\Delta x^2 Pe}$, F_k is Δt^2 times the average of F over the kth time interval Δt, and K_{fo} is Δt times the average of G (derivative of F) over the first time interval. Note that for memory functions that are singular at the origin, care must be taken to define this latter average K_{fo} as it is effectively a reaction rate and overshoot will occur if it is too large. Note also that by definition K_{fo} appears in F_k.

Appendix B: Conversion of MRMT to Integrodifferential Form of Equation (10)

Here we repeat previous results [*Carrera et al*., 1998; *Haggerty et al*., 2000] for completeness in our particular formulation with β factored out of the rate distribution of the MRMT, equations (14a) and (14b):

$$\frac{\partial c}{\partial t}+\beta\int_0^\infty f(\alpha)\frac{\partial s_\alpha(\alpha)}{\partial t}d\alpha+L[c]=0 \tag{B1a}$$

$$\frac{\partial s_\alpha(\alpha)}{\partial t}=\alpha c-\alpha s_\alpha \tag{B1b}$$

The second equation is solved by the integration factor method, substituting $s_\alpha=r_\alpha\exp(-\alpha t)$ into (B1b) and solving by direct integration treating c as external input function to obtain

$$r_\alpha(\alpha,t)=r_\alpha(\alpha,0)+\int_0^t c(t')\alpha\exp(-\alpha t')dt'$$

which upon back-substitution gives

$$s_\alpha(\alpha,t)=s_\alpha(\alpha,0)\exp(-\alpha t)+\int_0^t c(t')\alpha\exp(-\alpha(t-t'))dt'$$

Assuming zero initial immobile mass for simplicity, differentiating with respect to time, and inserting the result into [(B1a), yields

$$\frac{\partial c}{\partial t}+\beta\int_0^\infty f(\alpha)\frac{\partial}{\partial t}\left(\int_0^t c(t')\alpha\exp(-\alpha(t-t'))dt'\right)d\alpha+L[c]=0 \tag{B2}$$

and commuting the integrals gives

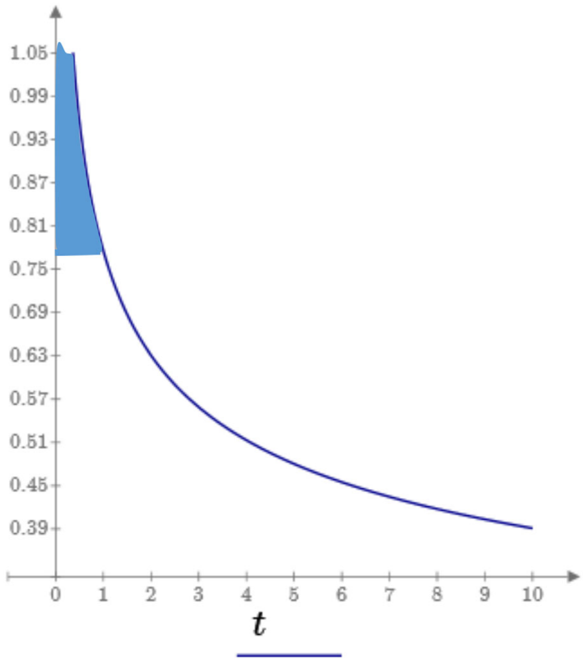

Figure A1. The tFADE memory function (curve) for the case $\gamma = 0.3$, and the PhEDEX approximation according to (C1)] in the case $\varepsilon = 1$ (the curve truncated at $t < \varepsilon$ below which the PhEDEX approximation is constant $\varepsilon^{-\gamma}/\Gamma(1-\gamma)$) with the density corresponding to equilibrium reaction shown as shaded region.

$$\frac{\partial c}{\partial t} + \beta \frac{\partial}{\partial t} \int_0^t c(t') \left(\int_0^\infty \alpha f(\alpha) \exp\left(-\alpha(t-t')\right) d\alpha \right) dt' + L[c] = 0 \tag{B3}$$

and defining the parenthetical quantity as *g*(*t*-*t'*) as in (15), we obtain (1).

Appendix C: PhEDEX Approximation of the tFADE Memory Function

The PhEDEX memory function approximating the tFADE case is as shown in equation (19) but for practical application the limit stops at some finite ε, and we write the PhEDEX memory function $g(t)$ as equal to $k_f(\varepsilon)$ for $t \le \varepsilon$, and as

$$g(t) = k_f(\varepsilon) \exp\left(- \int_\varepsilon^t \frac{\gamma}{\omega} d\omega \right) \tag{C1}$$

for $t > \varepsilon$. This ignores density of $g(t) - g(\varepsilon)$ on the interval $t \in [0, \varepsilon]$ that is shown as the shaded region in Figure Figure A1 in the case of $\varepsilon = 1$, where the unshaded region is $g(t)$ in equation (C1). Because this density corresponds to fast mass transfers, we treat it as if it occurs instantaneously and correct equation (C1) by adding a Dirac's function with area equal to the area A of the shaded region; that is, we replace (C1) with

$$g^o(t) \approx A\delta(t) + k_f(\varepsilon) \exp\left(- \int_\varepsilon^t \frac{\gamma}{\omega} d\omega \right) \tag{C2}$$

The area A is the integral of the shaded region, that is $A = \int_0^\varepsilon g(t)dt - \varepsilon g(\varepsilon)$ where $g(t) = t^{-\gamma}/\Gamma(1-\gamma)$ and is

$$A = \frac{\gamma \varepsilon^{1-\gamma}}{(1-\gamma)\Gamma(1-\gamma)}$$

To find the resulting retardation coefficient we write (C2) with the clunky but useful form

$$g^o(t) \approx A\delta(t) + k_f(\varepsilon) \exp\left(- \int_\varepsilon^t \frac{\gamma}{\omega} d\omega \right) \Phi(t-\varepsilon) + k_f(\varepsilon)[1 - \Phi(t-\varepsilon)] \tag{C3}$$

with which equation (1) becomes

$$R\frac{\partial c}{\partial t} + L[c] + \beta \frac{\partial}{\partial t}[g * c] = 0 \tag{C4}$$

where g is given again by (C1) and where $R = 1 + \beta A$.

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References

Berkowitz, B., S. Emmanuel, and H. Scher (2008), Non-Fickian transport and multiple-rate mass transfer in porous media, *Water Resour. Res.*, *44*, W03402, doi:10.1029/2007WR005906.

Bouchaud, J.-P., and A. Georges (1990), Anomalous diffusion in disordered media: Statistical mechanisms, models and physical applications, *Phys. Rep.*, *195*(4–5), 127–293.

Carrera, J., X. Sańchez-Vila, I. Benet, A. Medina, G. Galarza, and J. Guimerà (1998), On matrix diffusion: Formulations, solution methods and qualitative effects, *Hydrogeol. J.*, *6*, 178–190.

Coats, K. H., and B. D. Smith (1964), Dead-end pore volume and dispersion in porous media, *Soc. Pet. Eng. J.*, *4*, 73–84.

Dabros, T., and T. G. M. Van de Ven (1982), Kinetics of coating by colloidal particles, *J. Colloid Interface Sci.*, *89*, 232–246.

Dentz, M., and B. Berkowitz (2003), Transport behaviour of a passive solute in continuous time random walks and multirate mass transfer, *Water Resour. Res.*, *39*(5), 1111, doi:10.1029/2001WR001163.

Dentz, M., and D. M. Tartakovsky (2006), Delay mechanisms of non-Fickian transport in heterogeneous media, *Geophys. Res. Lett.*, *33*, L16406, doi:10.1029/2006GL027054.

Dentz, M., T. Le Borgne, A. Englert, and B. Bijeljic (2011), Mixing, spreading and reaction in heterogeneous media: A brief review, *J. Contam. Hydrol.*, *120–121*, 1–17.

Fernandez-Garcia, D., and X. Sanchez-Vila (2015), Mathematical equivalence between time-dependent single-rate and multirate mass transfer models, *Water Resour. Res.*, *51*, 3166–3180, doi:10.1002/2014WR016348.

Fiori, A., A. Zarlenga, H. Gotovac, I. Jankovic, E. Volpi, V. Cvetkovic, and G. Dagan (2015), Advective transport in heterogeneous aquifers: Are proxy models predictive?, *Water Resour. Res.*, *51*, 9577–9594, doi:10.1002/2015WR017118.

Fiori, A., A. Zarlenga, H. Gotovac, I. Jankovic, E. Volpi, V. Cvetkovic, and G. Dagan (2016), Reply to comment by S. P. Neuman on ''Advective transport in heterogeneous aquifers: Are proxy models predictive?'', *Water Resour. Res.*, *52*, 5703–5704, doi:10.1002/2016WR019209.

Ginn, T. R. (1999), On the distribution of generalized exposure-time in groundwater flow and reactive transport: Foundations: Formulations for groundwater age, geochemical heterogeneity, and biodegradation, *Water Resour. Res.*, *35*, 1395–1408.

Ginn, T. R. (2000a), On the distribution of multi-component mixtures over generalized exposure-time in subsurface flow and reactive transport: Theory and formulations for residence-time dependent sorption/desorption with memory, *Water Resour. Res.*, *36*, 2885–2894.

Ginn, T. R. (2000b), On the distribution of multi-component mixtures over generalized exposure-time in subsurface flow and reactive transport: Batch & column applications involving residence-time distributions and non-Markovian reaction kinetics, *Water Resour. Res.*, *36*, 2895–2904.

Ginn, T. R. (2009), Generalization of the multirate basis for time-convolution to unequal forward and reverse rates and connection to reactions with memory, *Water Resour. Res.*, *45*, W12419, doi:10.1029/2009WR008320.

Ginn, T. R., M. K. Nassar, T. Kamai, K. Klise, V. Tidwell, and S. McKenna (2013), On a recent solute transport laboratory experiment involving sandstone and its modeling, *Water Resour. Res.*, *49*, 7327–7338, doi:10.1002/2013WR013729.

Glassley, W. E., A. M. Simmons, and J. R. Kercher (2002), Mineralogical heterogeneity in fractured, porous media and its representation in reactive transport models, *Appl. Geochem.*, *17*, 699–708.

Haggerty, R., and S. M. Gorelick (1995), Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity, *Water Resour. Res.*, *31*, 2383–2400.

Haggerty, R., S. A. McKenna, and L. C. Meigs (2000), On the late-time behavior of tracer test breakthrough curves, *Water Resour. Res.*, *36*, 3467–3479.

Heidari, P., and L. Li (2014), Solute transport in low-heterogeneity sandboxes: The role of correlation length and permeability variance, *Water Resour. Res.*, *50*, 8240–8264, doi:10.1002/2013WR014654.

Lester, D. R., G. Metcalf, and M. G. Trefry (2014), Anomalous transport and chaotic advection in homogeneous porous media, *Phys. Rev. E*, *90*, 063012, doi:10.1103/PhysRevE.90.063012.

Luo, J., O. A. Cirpka, M. Dentz, and J. Carrera (2008), Temporal moments for transport with mass transfer described by an arbitrary memory function in heterogeneous media, *Water Resour. Res.*, *44*, W01502, doi:10.1029/2007WR006262.

Ma, R., C. Zheng, H. Prommer, J. Greskowiak, C. Liu, J. Zachara, and M. Rockhold (2010), A field-scale reactive transport model for U(VI) migration influenced by coupled multirate mass transfer and surface complexation reactions, *Water Resour. Res.*, *46*, W05509, doi:10.1029/2009WR008168.

Meerschaert, M. M., Y. Zhang, and B. Baeumer (2008), Tempered anomalous diffusion in heterogeneous systems, *Geophys. Res. Lett.*, *35*, L17403, doi:10.1029/2008GL034899.

Metzler, R., and J. Klafter (2000), The random walk's guide to anomalous diffusion: A fractional dynamics approach, *Phys. Rep.*, *339*, 1–77.

Neuman, S. P., and D. M. Tartakovsky (2009), Perspective on theories of anomalous transport in heterogeneous media, *Adv. Water Resour.*, *32*(5), pp. 670–680, doi:10.1016/j.advwatres.2008.08.005.

Neuman, S. P. (2016), Comment on ''Advective transport in heterogeneous aquifers: Are proxy models predictive?'' by A. Fiori et al., *Water Resour. Res.*, *52*, 5701–5702, doi:10.1002/2016WR019093.

Nkedi-Kizza, P., J. W. Biggar, H. M. Selim, M. T. van Genuchten, P. J. Wierenga, J. M. Davidson, and D. R. Nielsen (1984), On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated oxisol, *Water Resour. Res.*, *20*, 1123–1130.

Rao, P. S. C., R. E. Jessup, D. E. Rolston, J. M. Davidson, and D. P. Kilcrease (1980), Experimental and mathematical description of nonabsorbed solute transfer by diffusion in spherical aggregates, *Soil Sci. Soc. Am. J.*, *44*, 684–688.

Russian, A., M. Dentz, and P. Gouze (2016), Time domain random walks for hydrodynamic transport in heterogeneous media, *Water Resour. Res.*, *52*, 3309–3323, doi:10.1002/2015WR018511.

Sanz-Prat, A., C. Lu, R. T. Amos, M. Finkel, D. W. Blowes, and O. A. Cirpka (2016), Exposure-time based modeling of nonlinear reactive transport in porous media subject to physical and geochemical heterogeneity, *J. Contam. Hydrol.*, *192*, 35–49, doi:10.1016/j.jconhyd.2016.06.002.

Schumer, R., D. A. Benson, M. M. Meerschaert, and B. Baeumer (2003), Fractal mobile/immobile solute transport, *Water Resour. Res.*, *39*(10), 1296, doi:10.1029/2003WR002141.

Schumer, R., M. M. Meerschaert, and B. Baeumer (2009), Fractional advection-dispersion equations for modeling transport at the Earth's surface, *J. Geophys. Res.*, *114*, F00A07, doi:10.1029/2008JF001246.

Silva, O., J. Carrera, M. Dentz, S. Kumar, A. Alcolea, and M. Willmann (2009), A general real-time formulation for multi-rate mass transfer problems, *Hydrol. Earth Syst. Sci.*, *13*, 1399–1411.

Soler-Sagarra, J., L. Luquot, L. Martínez-Péreza, M. W. Saaltink, F. De Gasparia, and J. Carrera (2016), Simulation of chemical reaction localization using a multi-porosity reactive transport approach, *Int. J. Greenhouse Gas Control*, *48*, 59–68.

Wheeler, N. (1997), Simplified production of Dirac delta function identities, Reed College, Portland, Oreg. [Available at http://www.reed.edu/physics/faculty/wheeler/documents/index.html.]

Woolfenden, L., and T. R. Ginn (2009), Modeled groundwater age distributions, *Ground Water*, *47*(4), 547–557.

Zhang, Y., D. A. Benson, and D. M. Reeves (2009), Time and space nonlocalities underlying fractional-derivative models: Distinction and literature review of field applications, *Adv. Water Resour.*, *32*, 561–581, doi:10.1016/j.advwatres.2009.01.008.

Zhang, Y., C. Green, and B. Baeumer (2014), Linking aquifer spatial properties and non-Fickian transport in mobile-immobile like alluvial settings, *J. Hydrol.*, *512*(2014), 315–331.